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PREPARATION OF CARBODIIMIDES FROM THIOUREAS USING ORGANOLITHIUM OR ORGANOMAGNESIUM COMPOUND

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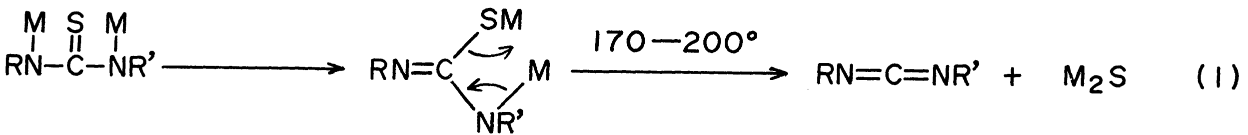
Thermal decomposition of N,N'-dilithio- or bis(bromomagnesio)-thioureas, prepared in situ from the thioureas substituted by bulky groups and butyllithium or bromoethylmagnesium, at 170-200°C under vacuum afforded dialkyl- or diaryl-carbodiimides in 33-61% yields. However, the decomposition of N,N'-dilithiothioureas was accelerated by the addition of carbon disulfide, and the carbodiimides were formed below room temperature in 67-87% yields.

Carbodiimides are usually prepared from thioureas and mercury(II) salts, or from phosgene derivatives such as isocyanates.[1-4] These synthetic methods use poisonous reagents as starting materials. We wish to report here transformation methods of thioureas to carbodiimides using butyllithium (BuLi in petroleum ether) or a Grignard reagent (EtMgBr in tetrahydrofuran), and to discuss the accelerating effect of carbon disulfide added in the reaction.

At first, N,N'-dimetallo-thioureas (1), prepared in situ from thioureas and two equivalents of BuLi or EtMgBr, were thermally decomposed under vacuum at 170-200° to afford the carbodiimides in 33-61% yields (Eq. 1). The results are summarized in Table 1.



1 (M = Li or MgBr) 2 3

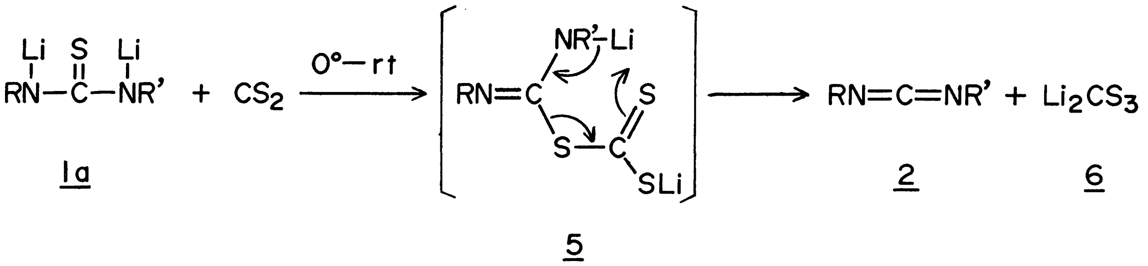
The sulfide, M_2S, was not isolated, but hydrogen sulfide was evolved by treatment of the distillation residue with water. The yields of carbodiimides prepared by thermal decomposition (Eq. 1) of the dilithio-derivatives (1; M=Li) were nearly the same as in the case of bis(bromomagnesio)-derivatives (1; M=MgBr) from thioureas having bulky alkyl or aryl groups. However, in the reaction of the dilithio-derivative having less-hindered group (1; M=Li, R=R'=4-$CH_3C_6H_4$), trace amount of 2 was formed, while 4-methylphenyl isothiocyanate was obtained in 27% yield in the reaction of the bis(bromomagnesio)-derivative (1; M=MgBr, R=R'=4-$CH_3C_6H_4$).

Table 1. Yield (%) of Carbodiimides by Thermal Decomposition of 1 (Eq. 1) and by the Reaction of 1 with Carbon Disulfide (Eq.2).

Thiourea used		Thermal Decompn.[a]		Reactn. with CS_2		Bp[e]	$\nu_{N=C=N}$
R	R'	M=Li	M=MgBr	M=Li[b,c]	M=MgBr[d]	°C/mmHg	cm^{-1}
2,6-$(CH_3)_2C_6H_3$	"	61	45	81	51	126-127/0.1	2150
2-$CH_3C_6H_4$	"	42	33	60	30	123-128/0.1	2145
$(CH_3)_3C$	"	39	38	60	-	60-65/30	2094
Cyclohexyl	"	60	40	87	-	100-105/0.1	2100
4-$CH_3C_6H_4$	"	trace	0[f]	trace	-	-	-
2,6-$(CH_3)_2C_6H_3$	C_6H_5	-	-	35	-	125-130/0.4	2132
2-$CH_3C_6H_4$	C_6H_5	-	-	20	-	140-145/0.7	2130

a) Yield of 2 by the thermal decomposition of 1 under vacuum at 170-200°C. b) Yield of 2 by the reaction of 1 (M=Li) with an equivalent amount of carbon disulfide in THF below room temperature. c) Under refluxing temperature in THF, the isothiocyanates were quantitatively formed.[5,6] d) Yield of 2 by the reaction of 1 (M=MgBr) with an excess of carbon disulfide for 6 h in THF under reflux. e) The structure of the carbodiimide prepared was determined by the comparisons of IR and NMR spectra and bp with those of an authentic sample. f) 4-Methylphenyl isothiocyanate was formed in 27% yield.

Secondly, the accelerating effect of carbon disulfide on the carbodiimide formation was examined (Eq. 2). The dilithio-derivatives (1a) were decomposed in the presence of carbon disulfide below room temperature to afford carbodiimides in better yields than in the absence of carbon disulfide at 170-200°C (see Table 1).



(2)

A typical procedure is described for the preparation of N,N'-bis(2,6-dimethylphenyl)carbodiimide: to a solution of the corresponding thiourea (4.4 g, 15 mmol) in dry tetrahydrofuran (40 cm^3), BuLi (33 mmol) was added dropwise under dry nitrogen atmosphere at room temperature.[7] Then, carbon disulfide (1.3 g, 17 mmol) was added slowly and the mixture was stirred for 10 min under cooling with ice-bath. The reaction mixture showed the characteristic $\nu_{N=C=N}$ band at 2150 cm^{-1} of the carbodiimide in the IR spectrum. Subsequently, solvent was quickly evaporated under vacuum and hexane (40 cm^3) was added to the residue to precipitate dilithium trithiocarbonate.[8] After removing the inorganic salt by filtration, the filtrate was distilled to afford N,N'-bis(2,6-dimethylphenyl)carbodiimide in 81% (3.1 g) yield; bp 126-127 °C/0.1 mmHg; IR (neat) 2150 cm^{-1} ($\nu_{N=C=N}$); NMR (CCl_4) δ=2.33 (s, 12, 2,6-$(CH_3)_2$), and 6.84 ppm (br. s, 6, arom.). The intermediate (5) could not be characterized, but it must be noted that the product mixture containing 2 and 6 was converted to the corresponding isothiocyanate by refluxing in tetrahydrofuran.[9]

On the contrary to the accelerating effect of carbon disulfide to form carbodiimides from dilithio-derivatives (1; M=Li), the reaction of bis(bromomagnesio)-thiourea (1; M=MgBr, R=R'=2-methyl or 2,6-dimethyl-phenyl) was not affected by the addition of excess amount of carbon disulfide, probably because the insertion reaction of carbon disulfide to Mg-S or Mg-N bond is difficult to occur under the reaction condition.

References and Notes

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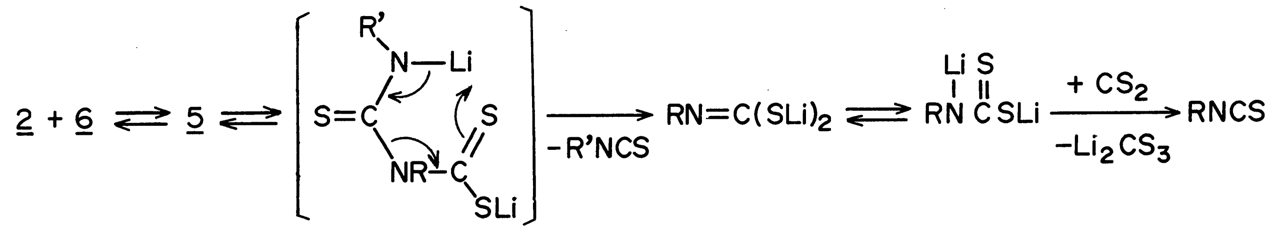
7) In the case of thermal decomposition (Eq. 1), the solvent was recovered and the residue was decomposed under vacuum at 170-200^{0}C.

8) Characterized by IR spectroscopy ($\nu_{CS_3^{2-}}$ (KBr) 936 cm^{-1}; ref.$^{10)}$ 905 cm^{-1}).

9) The carbodiimide (2; R=R'=2-methylphenyl) reacted exothermically with 6 in dry tetrahydrofuran at room temperature. After stirring for 30 min, $\nu_{N=C=S}$ (2070 cm^{-1} and $\nu_{N=C=N}$ (2146 cm^{-1}) bands were observed. The isothiocyanate was obtained in almost quantitative yield by heating the mixture for 4 h under reflux. The reaction course is tentatively proposed as follows.



The details of this reaction will be discussed in our separate paper.

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